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APPLIED ELECTROCHEMISTRY
AND CORROSION PROTECTION OF METALS

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Processing of Cadmium(II) Wastes from Battery Industry

V. V. Volynskii, A. V. Lopashev, I. A. Kazarinov, S. V. Grishin, and N. A. Solov'ev

*AIT Plant, Joint-Stock Company, Saratov, Russia
Saratov State University, Saratov, Russia*

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Abstract—Procedures allowing the use of cadmium electrodes from worked-out nickel–cadmium batteries as a secondary raw material in manufacture of the active paste for negative electrodes were developed and tested under industrial conditions at AIT Plant.

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The presently wide use and predictable high demand for alkaline nickel–cadmium batteries (NCBs) for industrial and household applications necessitate a search for economically efficient and environmentally safe methods for their utilization. Practical experience shows that one of ways to tackle this problem is to process the components of the active paste of alkaline NCBs to enable their repeated use [1]. The economic expediency of processing of the nickel oxide electrode is beyond any doubt, whereas the possible expenditure for storage, utilization, or processing of cadmium electrodes diminishes the commercial attraction of projects of this kind.

As a starting component of the active paste for the cadmium electrode serves CdO obtained by sublimation and oxidation of metallic Cd (Cd_{met}) in a cadmium-burning furnace at 700–800°C [2, 3]. On mixing CdO with activating additives, the content of Cd(II) in the active paste of cadmium electrodes varies from 40 to 70%, depending on the formula used in fabrication of active pastes [2, 3]. Metallic cadmium used to obtain CdO should conform to the requirements of GOST (State Standard) 1467–93, imposed on cadmium of Kd0 brand. The cost of Cd_{met} is determined by that of the cadmium-containing raw material and by the method used to produce Cd_{met} from this raw material. The high percentage content of Cd(II) in the active paste of cadmium electrodes suggests that their processing after the end of the service life of alkaline NCB is economically expedient. Simultaneously, this diminishes the probability of environment contamination by toxic cadmium compounds, which makes apparent the positive environmental aspect of this procedure.

Methods for processing of worked-out NCB electrodes are known; however, they do not allow repeated use of the raw material containing nickel and cadmium for production of components of active pastes [4, 5]. For example, worked-out electrodes of alkaline nickel–iron (cadmium) batteries are fused at 1450–1575°C to give nickel in the form of an alloy with iron [6]. A disadvantage of this method is that cadmium and nickel cannot be separated because Cd(II) is partly reduced at these temperatures, passes into the gaseous state, and is oxidized and carried away by discharge gases into the atmosphere, thereby contaminating the environment.

The aim of this study was to develop an economically efficient and environmentally safe technique for production of CdO from the active paste of cadmium electrodes of worked-out alkaline NCB by improving the efficiency of Cd_{met} recovery from the electrodes, diminishing the discharge of hazardous materials into the environment, and lowering the laboriousness and energy capacity of the process.

EXPERIMENTAL

To solve the problem formulated above, a laboratory installation for distillation of Cd_{met} was fabricated. It is shown schematically in Fig. 1. The installation operates on the pyrometallurgical principle, which consists in that cadmium waste is mixed with a reducing agent, with the subsequent heating of the mixture (stock) in an electric furnace without access of air [6].

Experiments were carried out with a stock containing 71.2% Cd(II). The component composition of the

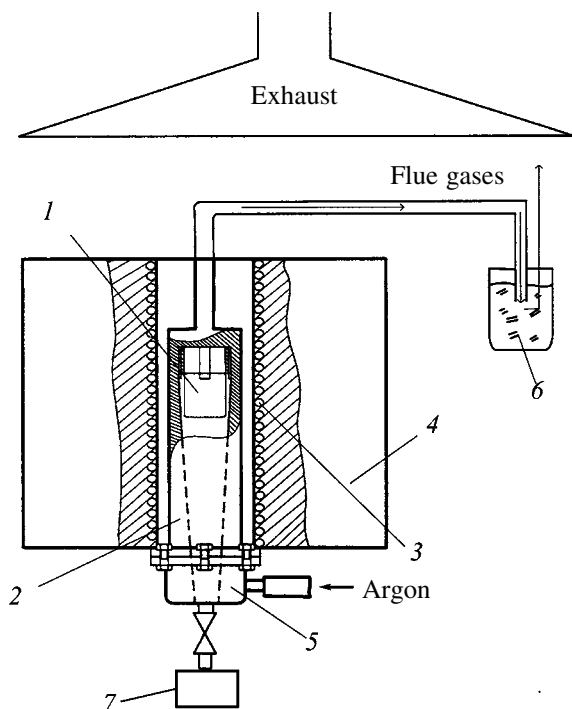


Fig. 1. Schematic of the installation for reduction of waste Cd(II): (1) reactor vessel, (2) solution, (3) heater, (4) furnace, (5) Cd_{met} collector, (6) water seal, and (7) dispenser vessel.

stock and the optimal conditions of the distillation process were found experimentally. As a criterion of quality of the process served such parameters as the reduction rate and recovery of Cd_{met}. It was found that these parameters strongly depend on the amount of stock present in the reaction zone. As can be seen in Fig. 2a, the reduction rate increases with the amount of stock in the working zone, whereas the recovery of Cd_{met} shows an opposite behavior (Fig. 2b).

The results of a chemical analysis of the stock after

Chemical composition of the stock with waste Cd(II) after distillation

Distillation	Content, %		
	Cd _{tot}	Ni _{tot}	Fe _{tot}
Primary	25	5.2	0.4
Secondary	0.06	58.4	0.3

primary and secondary distillation are listed in the table. The high residual content of Cd(II) in the stock after the primary distillation points to its incomplete recovery. However, repetition of the process enables virtually total reduction and recovery of Cd_{met} from the stock. The active pastes subjected to distillation contain nickel, and, therefore, the stock is enriched with this component in the course of thermal treatment.

Further, an industrial water-cooled groove furnace for processing of waste cadmium(II) was designed with account of the results obtained in the study and fabricated (Fig. 3).

The furnace includes a charging chamber 1, into which trays with the stock containing waste cadmium(II) are introduced. For convenience of charging, guiding rollers are mounted in the chamber. The door opening is sealed in the closed state with a rubber cord laid in a groove on the chamber door. An inspection window and an air cylinder 2 are situated on the edge surface of the charging chamber. The cylinder is intended for pushing the trays into the preliminary condensation chamber 3. The preliminary condensation chamber is separated from the charging chamber with a shutter attached to the shaft of an air cylinder 4, which is opened immediately before pushing in the trays. When closed, the shutter prevents discharge of hot flue gases into the shop at the instant when a tray

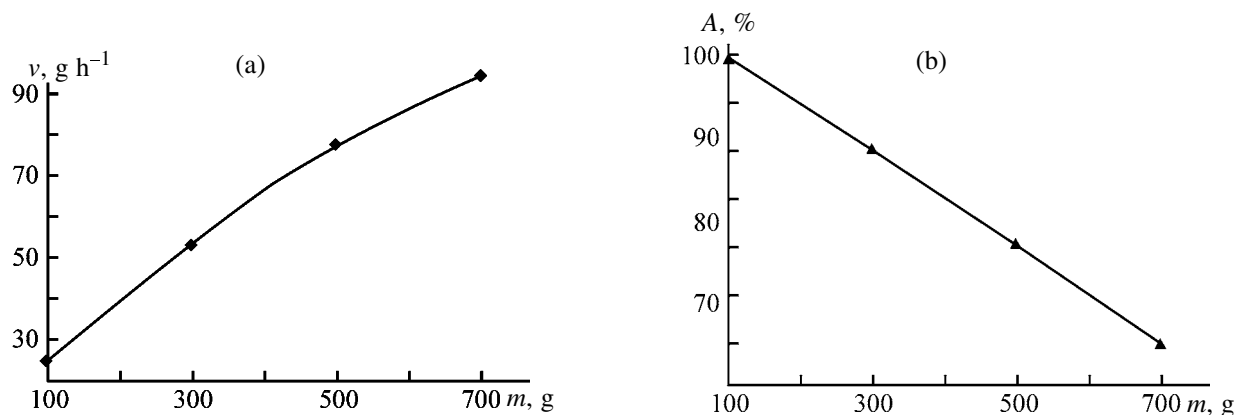


Fig. 2. (a) Cd_{met} recovery rate ν and (b) recovery A of metallic cadmium vs. the amount m of stock in the reaction zone.

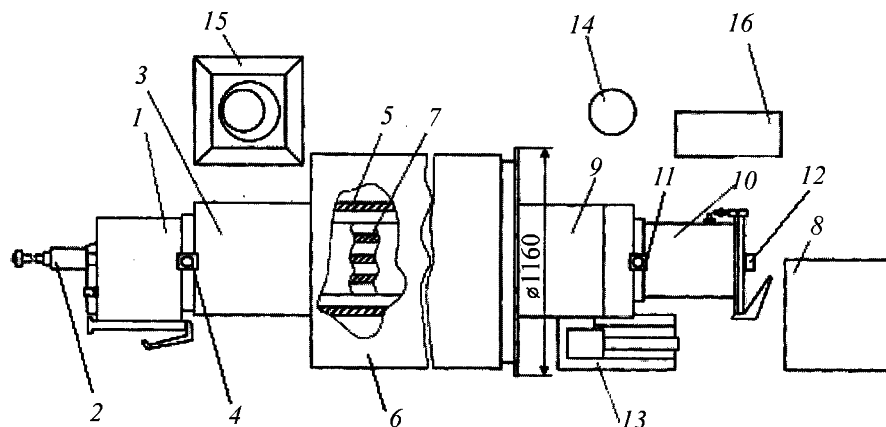


Fig. 3. Industrial water-cooled groove furnace for processing of waste cadmium(II). For explanations, see text.

with a stock is introduced into the charging chamber. The chamber walls are cooled by a water jacket.

A tray is moved from the preliminary condensation chamber into the muffle 5 of the heating chamber 6. The muffle lying on the base frame is welded from 8-mm-thick sheets of 12Cr18Ni10Ti stainless steel. The heat insulation of the muffle is made of lightweight refractory bricks and kaolin wool. At joints with the charging chamber the muffle is rigidly attached to the frame. The opposite end of the muffle is mounted on a movable support and can shift via thermal elongation. To make molten Cd_{met} or its vapors move in a certain direction, the muffle is inclined at an angle of 2° by the frame, with rotation by 5° about the muffle axis. Thermocouples are fixed in the central part of the upper and lower surfaces of the muffle. A heater 7 is mounted in a metallic case within the muffle. The furnace is heated by electric current passed through a heater in the form of a Nichrome wire coil on a ceramic tube. For insulation from the case, each of the coils of the three-phase heater is placed in a large-diameter ceramic tube. The tubes are mounted in sections of a hermetically sealed metallic box, which prevents Cd_{met} vapor from coming in contact with the heater. To monitor the reaction course and provide the prescribed reaction conditions, two more thermocouples are fixed on the inner surface of the upper plate of the heater. The analog signal from temperature sensors is converted on the real-time basis by a personal computer on the control stand 8 into the digital form, analyzed, and further used to operate thyristor controllers in order to maintain a prescribed temperature.

At the exit from the heating chamber, the muffle is jointed with the Cd_{met} vapor condensation chamber 9 and unloading chamber 10. Two air cylinders are

mounted in the unloading chamber, one 11 serves to move the carriage with a tray to be unloaded, and the other 12 controls the shutter hermetically separating the unloading and condensation chambers. Cd_{met} reduced by carbon arrives in the form of a vapor to the condensation chamber, to be cooled there and to be delivered into a discharge chamber equipped with its own ribbon heater and thermocouple. From the discharge chamber, liquid cadmium runs down into water in the collector tank 13, to form droplike particles.

The charging and unloading chambers are blown-through with argon from cylinder 14 in automatic mode. Because the working atmosphere in the heating chamber is reductive in the steady state, the whole heating chamber is blown-through with argon only at the beginning or end of furnace operation via charging and unloading chambers. The furnace is equipped with argon supply system. The operation of the gas pipes is monitored with three rotameters mounted on the gas panel. Flue gases are discharged through a water seal 15. By changing the water level in the water seal, a necessary excess pressure can be created in the chambers. To maintain a certain air pressure in the system of control over air cylinders, the furnace is equipped with an autonomous compressor 16.

The heating chamber and the charging and unloading chambers with condensation chambers are mounted on three separate frames welded from rectangular tubes. The power unit, gas distribution unit, air preparation unit, and water collector are mounted on the inner side of the frame and closed with decorative panels on their faces.

To distill off Cd_{met} according to the procedure developed, cadmium(II)-containing waste is screened,

separated from the metallic component, and mixed with P324 carbon (GOST 7885–86) [0.020–0.200 kg of carbon per 1 kg of Cd(I) contained in the active paste]. The resulting mixture is charged in batches in the continuous mode into the heating chamber of the furnace and kept at 650–1100°C without access of oxygen, with the charging interval determined for each batch with account of the time of its keeping at a prescribed temperature for 5–15 h. The output capacity of the furnace is, on the average, about 95 kg of Cd_{met} per 24 h and varies, depending on the type of waste being processed, in the range 70–120 kg in 24 h. In this case, the electric energy actually consumed by the furnace does not exceed values of about 7 kW h. The Cd_{met} obtained fully conforms in the content of impurities to the requirements of GOST 1467–93, imposed on cadmium of Kd0 brand:

Impurity	Content, %
Fe	0.0004
Pb	0.001
Cu	0.001
Ni	<0.001
Zn	0.001
Tl	<0.002
Mn	–

Gaseous reaction products, a mixture of carbon monoxide and carbon dioxide, pass through the water seal and are discharged into the environment without additional purification. Further, Cd_{met} is sublimed in a cadmium-burning furnace and oxidized with atmospheric oxygen to CdO. The resulting CdO is mixed with activating additives and used to fabricate cadmium electrodes for NCBs. The residual carbon containing cadmium compounds in an amount of 25 to 0.06% is accumulated and used to prepare sub-

sequent portions of a mixture of carbon with the active paste of cadmium electrodes of worked-out NCBs.

The technique suggested allows use of cadmium electrodes of worked-out alkaline NCB as a secondary raw material for production of CdO without use of toxic reagents; no industrial wastewater or environmentally hazardous gas discharges are formed.

CONCLUSIONS

(1) The technique suggested for utilization of cadmium electrodes of worked-out nickel–cadmium batteries provides a high efficiency of recovery of the expensive Cd_{met} for repeated use with any impact on the environment.

(2) Presently, the technique can only be used to process the industrial cadmium(II) waste from the battery industry in order to prevent its accumulation and to diminish the production cost of articles.

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